NOTE

Kyoko Saito Katsumata · Hiroyuki Shintani
Gyosuke Meshitsuka

Mechanism of detoxification of aluminum ions by kraft lignin treated with alkaline oxygen

Abstract Kraft lignins modified by radical sulfonation or alkaline oxygen treatment were rich in acidic groups, such as sulfonic acid, carboxylic acid, and phenolic hydroxyl groups, and were effective as soil-conditioning agents, especially because of their ability to trap aluminum ions eluted from soil under acidic conditions. Formation of complexes between aluminum ions and modified lignins was examined using potentiometric titration and ^{27}Al nuclear magnetic resonance (NMR) spectroscopy. Changes in the titration curve of a modified lignin by the addition of aluminum ions suggest the release of protons after the formation of complexes between them. Disappearance of ^{27}Al-NMR signals assigned to various aluminum ions by the addition of kraft lignin treated with alkaline oxygen was also attributed to the formation of complexes. The relative ease of proton release because of complex formation between a modified lignin and metal ions was as follows: $Fe^{3+} > Al^{3+} > Cu^{2+} > Pb^{2+} > Mn^{2+} > Ca^{2+}$. This indicates that aluminum complexes are quite stable, and the aluminum ion is not exchanged with cations other than Fe^{3+}.

Key words Aluminum ions · Alkaline oxygen-treated kraft lignin · Complex formation · Potentiometric titration · ^{27}Al-NMR

K.S. Katsumata (✉)[1]
Conservation Science Laboratory, Graduate School of Conservation for Cultural Property, Tokyo National University of Fine Arts and Music, Tokyo 110-8714, Japan

H. Shintani · G. Meshitsuka
Graduate School of Agricultural and Life Sciences, The University of Tokyo, Tokyo 113-8657, Japan

[1]*Present address*:
Asian Natural Environmental Science Center, The University of Tokyo, Yayoi, Bunkyo-ku, Tokyo 113-8657, Japan
Tel. +81-3-5841-7506; Fax +81-3-5841-5230
e-mail: ukyoko@mail.ecc.u-tokyo.ac.jp

Introduction

A high concentration of aluminum ions eluted from a soil matrix under acidic conditions is well known to have a seriously toxic effect on plant growth.[1–4] Aluminum ions eluted from a soil matrix at pH lower than 4.5 exhibits a serious negative effect on the elongation of plant root.[5,6] In natural forests the organic matter in soil is believed to remove this toxicity and to maintain the soil in a proper condition. In this context, it has been made clear from Fowrier transform-infrared (FT-IR) studies[7,8] that functional groups such as carboxylic and phenolic hydroxyl groups in soil organic matter form complexes with various metal ions.

In this study, new soil-conditioning agents were developed from softwood kraft lignin. We modified softwood kraft lignin by radical sulfonation or alkaline oxygen treatment to obtain a series of modified lignins rich in acidic groups, such as sulfonic acid and carboxylic acid groups. Humic substances are characterized as having carboxylic and other hydrophilic functions. Modified lignins prepared in the study were expected to be effective as soil-conditioning agents, especially by trapping aluminum ions eluted from soil.[9]

In a previous report, it was suggested that inhibiting the growth of radish (*Raphanus sativa* L. var. *radicula* Pers.) roots by aluminum ions eluted from soil (Toyoura test sand, pH 4.5–4.8) was successfully reversed by application of a kraft lignin treated with alkaline oxygen.[10] The negative effect of aluminum ions was also decreased in the case of cultivation of plants in culture solution by adding a modified lignin at pH 4.5.[10,11] Although the soluble aluminum ions in the culture solution were at a markedly high level, radish root elongation was not obviously inhibited when a large amount of modified lignin was applied. These results suggested that toxicity of aluminum ions to plants could be reduced by the formation of complexes between aluminum ions and acidic groups in the modified lignins.

In this report the formation of complexes between aluminum ions and acidic groups of a modified lignin in the

solution was examined using potentiometric titration and [27]Al nuclear magnetic resonance (NMR) spectroscopy.

Experimental

Chemical modification of softwood kraft lignin

Commercial softwood kraft lignin purified with dioxane–diethyl ether was treated with alkaline oxygen or alkaline oxygen with Na_2SO_3, as shown in a previous report.[9] To prepare L-4·ND, the reaction mixture treated with alkaline oxygen for 4h was deionized using a cation-exchange resin (Amberlite IR120B; Organo, Tokyo, Japan) to remove any excess alkali; the eluate was adjusted to around pH 7 using dilute KOH and dilute HNO_3. Sample names and treatment conditions are shown in Table 1.

Titration of modified lignins

Titration in the absence of aluminum ions

Free type modified lignins that did not contain sodium ions were prepared by the following method. A modified lignin (ca. 2g) was dissolved in 50ml of water or 0.1M KOH solution and eluted through a cation-exchange column (Amberlite IR120B); then the eluate volume was adjusted to 200ml with water. The solution (5ml) was evaporated to dryness, and the dry weight of the lignin sample was measured to determine the exact lignin concentration.

A solution containing lignin sample (≥100mg) was titrated with 0.1M KOH under a nitrogen stream at room temperature. An autotitrator (COMTITE-550; Hiranuma, Tokyo, Japan) with a combination electrode (GR-522) together with a metallic electrode (TPT-351) was used for simultaneous measurements of pH and conductivity.

Titration in the presence of aluminum ions

Solutions of 5, 10, and 20mM Al^{3+} and solutions of 5mM Ca^{2+}, Pb^{2+}, Mn^{2+}, Cu^{2+}, and Fe^{3+} were prepared from $Al(NO_3)_3 \cdot 9H_2O$, $Ca(NO_3)_2 \cdot 4H_2O$, $Pb(NO_3)_2$, $Mn(NO_3)_2 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, and $Fe(NO_3)_3 \cdot 9H_2O$, respectively. KNO_3 (6.07g) was dissolved in 100ml of water. The solution of metal ion (5ml) was added to the aqueous solution of modified lignin (100mg). The KNO_3 solution (5ml) was then added to control the ionic strength. Finally, the volume of the solution was adjusted to 30ml. The mixture was potentiometrically titrated with 0.1N KOH under a nitrogen stream at room temperature using an autotitrator (COMTITE-550) with a combination electrode (GR-522).

^{27}Al NMR

A modified lignin, L-8 (0–20mg), was dissolved in water (1ml), and Al^{3+} (5μmol) was added. The mixture was adjusted to a desired pH of 4.1–5.2 with dilute KOH (ca. 10mM) or dilute HNO_3 (ca. 10mM). The mixture was filtered through a glass wool filter to remove the precipitate and then transferred into a tube for ^{27}Al-NMR measurement. The total concentration of aluminum ions in the solution was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) (JY 70 PLUS; Rigaku, Japan). Acetone-d_6 solution saturated with potassium hexathiocyanatoaluminate(III) {$K_3[Al(NCS)_6]$} according to a procedure described by Komatsu and coworkers,[12] was used as an external standard. ^{27}Al-NMR spectra were recorded on a Bruker AC 300 NMR spectrometer at ambient temperature without spinning. The measurement was run using a 10mm (o.d.) tube, and the proton signal of acetone-d_6 in a capillary for the external standard was used as locking signal.

Solutions of Al^{3+} (1 and 5mM) at pH 3.0 were also used for ^{27}Al-NMR measurements. The ratio of the peak areas of the $Al(H_2O)_6^{3+}$ resonance at 0ppm and the $Al(NCS)_6^{3-}$ resonance at −33.9ppm was used to calibrate the concentration of each form of the aluminum ion.

Results and discussion

Characterization of modified lignin

Acidic groups in modified lignins were classified into four groups (one strongly acidic group, three weakly acidic groups) by the simultaneous titration of pH (potentiometry) and conductivity (conductometry). Titration curves of pH and conductivity for modified lignin with radical sulfonation (S-1) are shown in Fig. 1. The first acidic group, which had strong acidity similar to HCl, was detected for a kraft lignin treated by radical sulfonation and lignosulfonate (LSA). It seems reasonable to believe that sulfonic

Table 1. Sample preparation conditions

Sample	Lignin (g/l)	Na_2SO_3 (g/l)	O_2 pressure (MPa)	Temperature (°C)	Time (h)	Treatment
KL	20	0	Atm.	RT	–	Control
L-4	20	0	0.3	70	4	Alkali-oxygen
L-4·ND	20	0	0.3	70	4	Alkali-oxygen, no dialysis
L-8	20	0	0.3	70	8	Alkali-oxygen
S-1	20	50	0.3	70	4	Radical sulfonation
LSA	–	–	–	–	–	Lignosulfonate

RT, room temperature; Atm., atmorpheric; KL, keaft lignin; LSA, lignosulfonate

acid groups in those lignins correspond to this type of acidic group. Even a trace amount of this group was not found in the original kraft lignin in modified kraft lignins by alkali-oxygen treatment (Table 2). Weak acid I was a relatively strong acidic group, which might be mainly attributed to carboxylic groups. Weak acid II was considered to include not only some carboxylic groups but also the first dissociation of catechol type structure because of the presence of the latter structure in kraft lignins. Catechol groups are expected to be produced by the partial demethylation during kraft cooking.[13] Weak acid III corresponds to regular phenolic hydroxyl groups in the original and modified kraft lignins. It is important that the determination of each acidic group in the modified lignin was accomplished much more successfully by the simultaneous measurements of pH and conductivity used in this study than by the conductivity only noted in the previous report.[9]

As shown in Table 2, the amount of weak acid II increased with the increase in reaction time of alkaline oxygen treatment, but the amount of weak acid I decreased (see KL, L-4, and L-8). Because the formation of aliphatic carboxylic acids is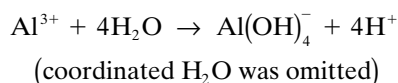 believed to be one of the main reactions during alkaline oxygen treatment, the increase in weak acid II can be explained by the formation of these acids. Weak acid I could be assigned to be carboxylic acid attached to an aromatic nucleus, because of the decrease to some extent by degradation of aromatic structures. The decrease in weak acid III was also explained by the degradation of free phenolic aromatic rings during alkaline oxygen treatment.

Formation of a complex between modified kraft lignin and aluminum ions

Aluminum toxicity to radish cultivated in culture solution was removed by adding modified lignins as reported in the previous study.[10,11] To understand the effectiveness of modified lignin, it is essential to obtain the information about the interaction between a modified lignin and aluminum ions. Potentiometric titration curves and pKa values for a solution containing the kraft lignin treated with alkaline oxygen for 8h (L-8) and various amounts of Al^{3+} are shown in Fig. 2 and Table 3, respectively.

Formation of complexes between L-8 and aluminum ions was suggested by the lower pH of a solution with aluminum ions than without Al^{3+} (Fig. 2). It is well known that the proton is released by the formation of a coordinate complex between a ligand and acidic groups, (e.g., carboxylic acid groups and metal ions).[14] Even in the case of adding 0.107mmol of aluminum ions to about 100mg of L-8, however, the amount of aluminum ions was not sufficient to form complexes with all the acidic groups in L-8. Some protons that originate in the acidic groups remain without forming complexes.

Here, the hydrolysis of an aluminum ion is known as the formation of $Al(OH)_4^-$ together with protons from an aluminum ion, as shown by following equation.

$$Al^{3+} + 4H_2O \rightarrow Al(OH)_4^- + 4H^+$$

(coordinated H_2O was omitted)

The potentiometric titration curve for aluminum only [0.027mmol $Al(NO_3)_3$] shown in Fig. 2 started from pH 4.2, with the pH sharply increasing with only a small amount of KOH; its differentiation curve (Fig. 2e) has inflection points at pH 4.8 and 8.8. On the other hand, the titration curve for L-8 started from a much lower pH (ca. pH 3), and at least two inflection points were observed in the differentiation curve (Fig. 2a) at pH 3.5 and 5.3, which indicate pKa values of acidic groups in L-8. Another acidic group of pKa 9.0 was
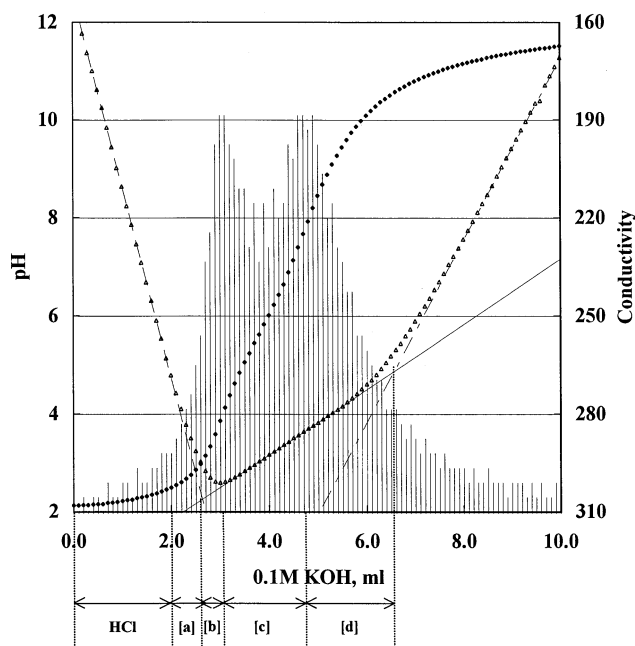

Fig. 1. Titration curves of S-1 for pH and conductivity. S-1: 153.6mg. *Squares*, titration curve for pH; *triangles*, titration curve for conductivity; [*a*], strong acid; [*b*], weak acid I; [*c*], weak acid II; [*d*], weak acid III

Table 2. Acidic groups in lignin samples

Lignin	Strong acid	Weak acid I	Weak acid II	Weak acid III	Total
KL	–	0.11	0.26	0.26	0.63
L-4	–	0.07	0.31	0.19	0.57
L-8	–	0.08	0.40	0.19	0.68
S-1	0.08	0.05	0.22	0.24	0.59
LSA	0.21	0.08	–	0.18	0.47

Each acidic group (eq./200g lignin) was determined as shown in Fig. 1

expected by conductometric titration. We assumed that these pKa values correspond to those of weak acids I, II, and III, respectively. When small amounts of aluminum ions (0.027 mmol/0.1 g lignin sample) are added, there should be no inflection point corresponding to free alumi-num ions; and, in fact, all inflection points were slightly different from those of L-8 (Table 3), and the amount of the acidic groups of weak acid I increased markedly. This indicates a relatively strongly acidic nature of the initially formed lignin–aluminum complex. When the dosage of aluminum ions was increased to 0.053 mmol/0.1 g lignin, the amount of the acidic group with pKa 3.5 increased further. A marked increase in weak acid III was detected together with the new appearance of an acidic group with pKa 4.0 using a dosage of 0.107 mmol Al^{3+}/0.1 g lignin.

It was reported that hydroxide ion readily combines with Al^{3+} at pH 5–7 to form $Al^{2+}OH$–EDTA.[15] It was also found that $Al^{2+}OH$–EDTA did not consume further alkali below pH 10. In the case of some humic substances, it was suggested that alkali consumption by coordinated aluminum was not obvious around pH 9.[15] Based on these facts, maximum alkali consumption by the formation of complexes of aluminum ions and acidic groups in lignin could be equimolar with the amount of aluminum ions. In other words, Al–acidic group complexes formed in lignin may behave as so-called monobasic acids against titration. If all aluminum ions of 0.027 mmol combine with acidic groups in 100 mg of lignin, aluminum ions could consume 0.027 mmol of hydroxide ions as a maximum together with proton release by the coordination with acidic groups. Because the total amount of acidic groups was determined to be 0.34 mmol in 100 mg of L-8 (Table 3), the increase in total acid by adding 0.027 mmol of aluminum to 100 mg of L-8 (0.08 mmol) may indicate the degree of hydroxylation of aluminum ions in lignin–aluminum complexes.

Complexes between aluminum ions and L-8 would not be stable at pH 9 or higher, and aluminum species produced by decomposition of complexes would consume further alkali. This is part of the reason for higher alkali consumption at aluminum dosages of 0.053 and 0.107 mmol/100 mg of L-8.
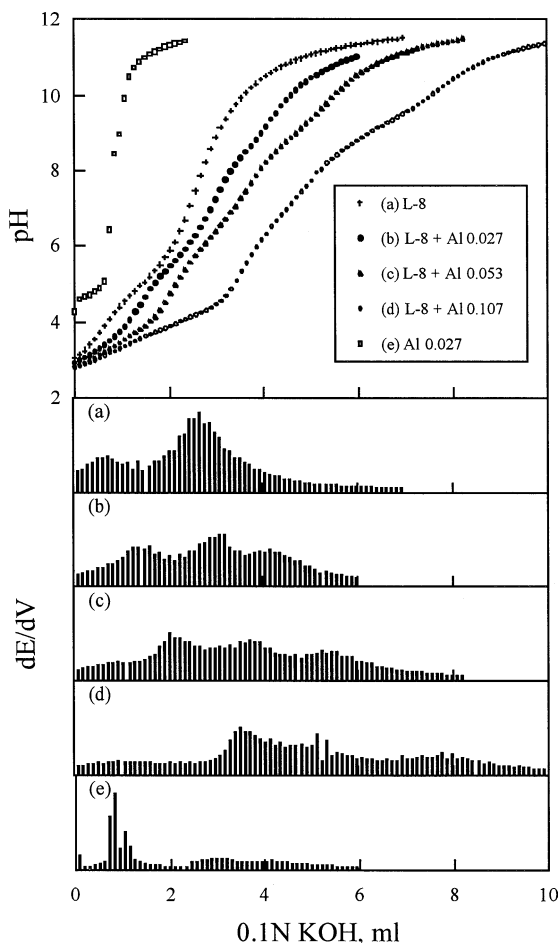
Comparison of various modified lignins

The results of complex formation between aluminum ions and L-4, which was done under mild conditions, were basi-

Fig. 2. Potentiometric titration curves for lignin L-8 in the presence of various amounts of aluminum ions. L-8: *a–d*, 100 mg; *e*, 0 mg. Al^{3+}: *a*, 0 mmol; *b*, *e*, 0.027 mmol; *c*, 0.053 mmol; *d*, 0.107 mmol

Table 3. pKa Values of complexes between a modified kraft lignin and aluminum ions at various Al/modified lignin ratios

Modified lignin[a]	Al^{3+} (mmol)	pKa (alkali consumption, mmol), at inflection point[b]				Total alkali consumption (mmol)
		1	2	3	4	
L-8	–	3.5 (0.075)	–	5.3 (0.192)	9.0 (0.075)	0.342
	0.027	3.4 (0.139)	–	5.8 (0.182)	8.6 (0.096)	0.417
	0.053	3.5 (0.203)	–	6.2 (0.171)	10.0 (0.176)	0.550
	0.107	3.0 (0.096)	4.0 (0.256)	6.8 (0.160)	9.9 (0.470)	0.983
L-4·ND	–	2.8 (0.056)	3.6 (0.167)	5.9 (0.116)	9.5 (0.126)	0.466
	0.024	2.9 (0.145)	3.2 (0.078)	6.1 (0.184)	8.6 (0.078)	0.484
	0.048	2.9 (0.165)	4.5 (0.174)	6.7 (0.116)	8.8 (0.145)	0.601
	0.097	2.8 (0.165)	4.2 (0.271)	6.9 (0.136)	9.0 (0.213)	0.785
S-1	–	2.8 (0.040)	3.7 (0.050)	5.8 (0.080)	9.2 (0.120)	0.291
	0.025	2.9 (0.070)	4.0 (0.080)	6.3 (0.080)	8.6 (0.120)	0.351
	0.050	2.9 (0.090)	4.1 (0.120)	5.8 (0.140)	9.2 (0.100)	0.451
	0.100	2.8 (0.070)	4.1 (0.281)	7.1 (0.090)	9.1 (0.190)	0.631

[a] Modified lignin: 100 mg
[b] Inflection point of the differentiation curve of the potentiometric titration were numbered from the acid side

cally similar to those for L-8 (data not shown). In the case of kraft lignins, the pH change after addition of aluminum ions was greater than those of L-4 and L-8. This was expected based on a model experiment using a pyrocatechol whose structure is believed to be present in the original kreft lignins and to have good ability to form complexes with metal ions. However, the contribution of the catechol structure is limited in the case of a modified lignin with alkali-oxygen because this type of structure would be readily decomposed during modification.

A modified lignin without dialysis (L-4·ND) characteristically had much lower pKa values even in the absence of aluminum ions, as shown in Table 3 (pKa 2.8), than those of the dialyzed sample, L-4 (pKa 3.6). Proton release with pKa 2.8 increased in the presence of 0.024 mmol of aluminum ions (0.056–0.145 mmol). This must be due to the presence of low-molecular-weight organic acids, such as oxalic acid, which have a strong tendency to achieve complex formation with aluminum ions. Incidentally, oxalic acid is one of the low-molecular-weight organic acids secreted from plant roots as a response to aluminum toxicity.[16–18] Secretion of oxalate was reported in the case of taro (*Calocasia esculenta* L, Bun-long and Lehna maoli)[16] and buckwheat (*Fagopyrum esculentum* Moench, cv. Jianxi).[18,19] Much research has been reported on the reduction of aluminum toxicity by oxalic acid.[18]

As shown in Fig. 3 and Table 3, the strongly acidic group in sulfonated kraft lignin (S-1) increased markedly after addition of aluminum ions. The means of coordination with aluminum ions to release protons of such high acidity is not clear. In this context, coordination with an *ortho*-sulfonated phenolic structure proposed by Meshitsuka and Nakano[19,20] must be examined carefully.

Sulfonic acid groups in lignosulfonate (LSA) are strongly acidic even without metallic ions, and no particular change in the strongly acidic group was observed after addition of aluminum ions (data not shown). Therefore, it is not yet possible to discuss whether the sulfonic acidic group in LSA participates in complex formation. Because the pKa value of weak acid II of LSA was lower when aluminum ions were added, the weakly acidic groups in LSA would be participating in the formation of complexes with aluminum ions. The reduction of aluminum toxicity achieved by adding a large amount of LSA, as reported in our previous paper[11] would be explained by this phenomenon.

Effect of amount of modified lignin and pH on complex formation

Aluminum ions in aqueous solution gave clear, sharp peaks at 63 ppm and a weak peak at 0 ppm in the ^{27}Al-NMR spectrum (Fig. 4). Peaks at 0 and 63 ppm are assigned mainly to $Al(H_2O)_6^{3+}$ and the center aluminum atom of $AlO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$, respectively.[21,22] The peak at −33.4 ppm corresponded to $Al(NCS)_6^{3-}$ in acetone-d_6 as an external standard.[12] The concentration of Al_{13} species at pH 4.5 was calculated by multiplication of 13 by the value determined from the peak at 63 ppm, because only one center Al
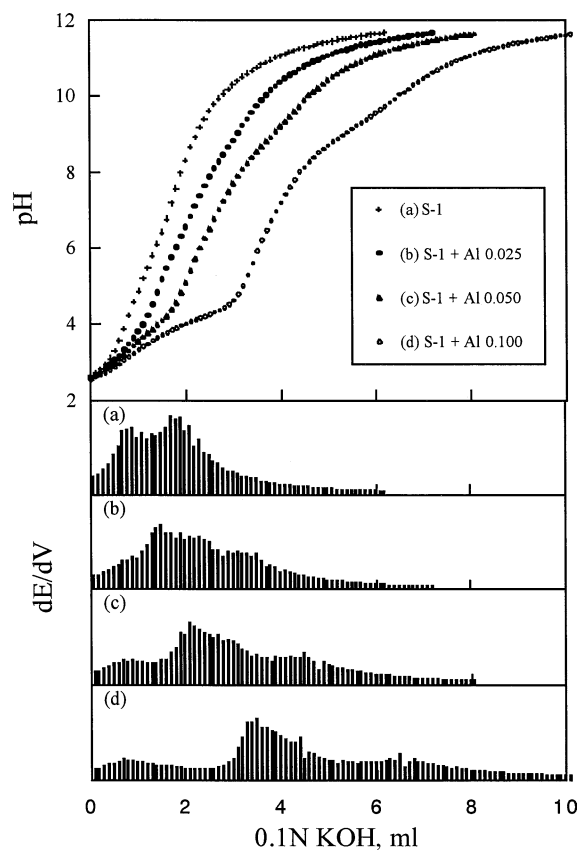
Fig. 3. Potentiometric titration curves for S-1 in the presence of various amounts of aluminum ions. S-1, 100 mg. Al^{3+}: *a*, 0 mmol; *b*, 0.025 mmol; *c*, 0.050 mmol; *d*, 0.100 mmol
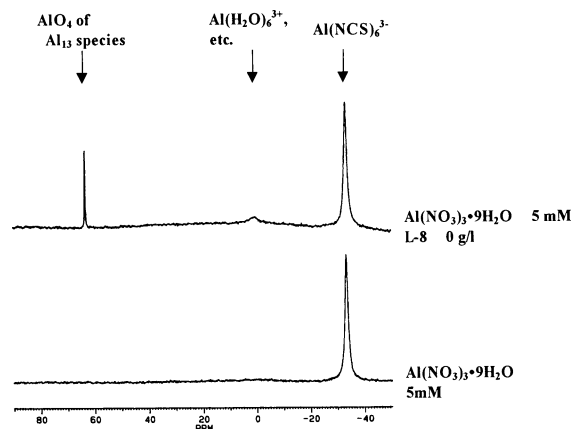
Fig. 4. Effect of lignin L-8 on ^{27}Al-NMR spectrum of aqueous aluminum solution

atom of the Al_{13} species was detected here. However, the total amount of aluminum ions determined from the peaks at 0 ppm and 63 ppm was different from the absolute amount of the soluble aluminum ions determined by ICP-AES even in the case of no addition of L-8 (Table 4). The total amount determined by NMR was slightly higher than the amount found by ICP-AES at lower pH (around 4.1) (not shown). The presence of some soluble Al species that

Table 4. Effect of concentration of L-8 on Al species in aqueous solution

L-8 (mg/ml)	Al[a] (μmol/ml)		
	ICP[b]	63 ppm[c]	0 ppm[d]
0	4.4	2.23	0.21
0.5	0.3	0.15	0.09
1.0	0.5	0.21	0.20
2.0	0.3	0.10	0.13
5.0	0.0	0	0
10.3	1.2	0	0
14.9	4.1	0	0
19.9	4.9	0	0

[a] $Al(NO_3)_3 \cdot 9H_2O$: 5.02 μmol/ml
[b] Concentration was determined by ICP-AES
[c] Concentration of aluminum of Al_{13} polymer at 63 ppm was determined by comparing the peak area to that of the ^{27}Al-NMR resonance of $Al(NCS)_6^{3-}$
[d] Concentration of monomeric aluminum species at 0 ppm was determined by comparing the peak area to that of the ^{27}Al-NMR resonance of $Al(NCS)_6^{3-}$

could not be detected by ^{27}Al-NMR was also considered at pH higher than 4.5.

The spectra of ^{27}Al-NMR were examined to obtain further information about the formation of complexes between aluminum ions and L-8 at pH 4.5. The signals at 0 and 63 ppm decreased when a small amount of a modified lignin was added and finally disappeared completely when 20 mg of L-8 was added to 1 ml of 5 μmol aluminum solution, although a considerable amount of aluminum ions were present in solution (Fig. 4, Table 4). It is known that a sharp resonance is observed only when ligands of an aluminum ion are symmetric.[23] However, the complex between lignin and aluminum ions cannot be symmetric, so the signals of aluminum ions in the complex become significantly broad and are involved in the baseline of the spectrum.

Formation of complexes between modified lignin and various metal ions

Formation of complexes between modified lignins (L-4, L-4·ND, S-1, LSA) and various metal ions were examined by potentiometric titration. The modified kraft lignin treated with alkali-oxygen for 4 h (L-4) appeared to form a complex quite readily with Fe^{3+}, and the complex seemed stable even at high pH (up to pH 11) because of lack of inflection in the differentiation curve obtained from the titration curve in this pH range. Proton release was detected for the case of Cu^{2+}, and formation of weak complexes was observed for Pb^{2+} but not for Mn^{2+}.

Ease of proton release from complexes between modified lignins and metal ions was in the order of $Fe^{3+} > Al^{3+} > Cu^{2+} > Pb^{2+} > Mn^{2+} > Ca^{2+}$. This order was the same as the stability of complexes between fulvic acid and various metal ions reported by Schnitzer and Hoffman.[24,25] Because the complexes between modified lignin and aluminum ions were strong, it was difficult to exchange the aluminum ions in the complexes with other cations. Shinagawa and coworkers reported that the cation-exchange capacity (CEC) of humic acid decreased with increasing amount of aluminum ions.[26]

To apply a modified lignin to fields of acidic soil as a soil-conditioning agent, sufficient modified lignins are required not only to remove aluminum ions but also to retain essential metal ions for plant growth and to maintain an adequate pH.

L-4·ND released protons by the formation of complexes even with Mn^{2+} (data not shown), suggesting that low-molecular-weight organic acids in L-4·ND could form complexes with Mn^{2+}. This suggests that a more effective modified lignin to remove aluminum toxicity can be obtained by improving the purification method.

Conclusions

The formation of complexes between aluminum ions and modified lignins was examined using potentiometric titration and ^{27}Al-NMR spectroscopy. Changes in the titration curve of a modified lignin by adding aluminum ions suggest the release of protons due to the formation of complexes between them. The disappearance of ^{27}Al-NMR signals assigned to various aluminum ions after adding L-8 was attributed to the formation of complexes. Modified lignins that contained much muconic acid and catechol-type structures exhibited significant proton release by forming complexes with aluminum ions.

Low-molecular-weight organic acids in L-4·ND showed strong ability to form complexes with aluminum and other metallic ions. This suggests that more effective modified lignin to remove aluminum toxicity can be obtained by improving the purification method.

The order of proton release from complexes between a modified lignin and metal ions was as follows: $Fe^{3+} > Al^{3+} > Cu^{2+} > Pb^{2+} > Mn^{2+} > Ca^{2+}$. This indicates that complexes of aluminum ions are quite stable and aluminum ions are not exchanged with cations other than Fe^{3+}.

References

1. Sparks DL (1995) The chemistry of soil acidity. In: Environmental Soil Chemistry. Academic Press, San Diego, pp 203–217
2. Saigusa M, Shoji S, Takahashi T (1980) Plant root growth in acid andosols from northeastern Japan. 2. Exchangeable acidity Y1 as a realistic measure of aluminum toxicity potential. Soil Sci 130:242–250
3. Foy CD (1984) Physiological effects of hydrogen, aluminum, and manganese toxicities in acid soil. In: Adams F (ed) Soil acidity and liming. Agronomy monograph 12, 2nd edn. American Society of Agronomy, Crop Science Society of America, Soil Science Society of America, Madison, WI, pp 57–97
4. Magistad OC (1925) The aluminum content of the soil solution and its relation to soil reaction and plant growth. Soil Sci 20:181–225
5. Foy CD, Chaney RL, White MC (1978) The physiology of metal toxicity in plants. Annu Rev Plant Physiol 29:511–566
6. Wagatsuma T, Kaneko M, Hayasaka Y (1987) Destruction process of plant root cells by aluminum. Soil Sci Plant Nutr 33:161–175
7. Tan KH (1978) Formation of metal–humic acid complexes by titration and their characterization by differential thermal analysis and infrared spectroscopy. Soil Biol Biochem 10:123–129

8. Schnitzer M, Skinner SIM (1963) Organo-metallic interactions in soils. 1. Reactions between a number of metal ions and the organic matter of a podzol Bh horizon. Soil Sci 96:86–93

9. Saito K, Nakanishi TM, Matsubayashi M, Meshitsuka G (1997) Development of new lignin derivatives as soil conditioning agents by radical sulfonation and alkaline-oxygen treatment. Mokuzai Gakkaishi 43:669–677

10. Katsumata SK, Maruyama M, Meshitsuka G (2001) Reduction of aluminum toxicity to radish by alkaline oxygen treated kraft lignin. J Wood Sci 47:129–134

11. Katsumata SK, Shintani H, Meshitsuka G (2000) Development of new lignin derivatives as soil conditioning agents. In: Proceedings of international symposium on cellulose and lignocellulosics chemistry 2000 (ISCLC), Kunming, China, December 2000, pp 149–152

12. Komatsu N, Yokoi, Kubota E (1988) An ^{27}Al NMR study on the complexes present in the solutions of potassium hexathiocyanato-aluminate(III). Bull Chem Soc Jpn 61:3746–3748

13. Falkehag SI, Marton J, Adler A (1966) Chromophores in kraft lignin. Adv Chem Ser 59:75–89

14. Vance GF, Stevenson FJ, Sikora FJ (1996) Environmental chemistry of aluminum–organic complexes. In: Sposite G (ed) Environmental chemistry of aluminum. CRC Press, Boca Raton, FL, pp 169–220

15. Yoshida M, Nakao Y (1971) Behavior of aluminum–humic acid complexes as revealed by titration curves (in Japanese). J Sci Soil Manure Jpn 42:333–337

16. Ma Z, Miyasaka SC (1998) Oxalate exudation by taro in response to Al. Plant Physiol 118:861–865

17. Ma JF, Zheng SJ, Matsumoto H (1997) Detoxyfying aluminum with buckwheat. Nature 390:569–570

18. Ma JF, Hiradate S, Matsumoto H (1998) High aluminum resistance in buckwheat. II. Oxalic acid detoxifies aluminum internally. Plant Physiol 117:753–759

19. Meshitsuka G, Nakano J (1980) Studies on water solubilization of lignin (1). Jpn TAPPI 34:349–355

20. Meshitsuka G, Nakano J (1980) Studies on water solubilization of lignin (2). Jpn TAPPI 34:743–749

21. Akitt JW, Greenwood NN, Lester GD (1969) Hydrolysis and dimerisation of aqueous aluminium salt solutions. Chem Commun 988–989

22. Akitt JW, Greenwood NN, Khandelwal BL, Lester GD (1972) ^{27}Al nuclear magnetic resonance studies of the hydrolysis and polymerisation of the hexa-aquo-aluminium(III) cation. J Chem Soc Dalton 604–610

23. Delpuech JJ (1983) Aluminum-27. In: NMR of Newly Accessible Nuclei, vol 2. Academic Press, San Diego, pp 153–195

24. Schnitzer M (1969) Reaction between fulvic acid, a soil humic compound and inorganic soil constituents. Soil Sci Soc Am Proc 33:75–81

25. Schnitzer M, Hoffman I (1967) Thermogravimetric analysis of the salts and metal complexes of a soil fulvic acid. Geochim Cosmochim Acta 31:7–15

26. Shinagawa A, Miyauchi N, Higashi T (1982) Preparation of Al-humates and their aluminum content and cation-exchange capacity. Soil Sci Plant Nutr 28:1–7